Method for the deposition of an alloy on a substrate

The invention relates to a method for the deposition of an alloy on a substrate.

There are various known methods for applying layers to a substrate. These include, for example, plasma spraying, electrodeposition or vapor deposition processes, inter alia.

An article by G. Devaray im Bulletin of Electrochemistry 8 (8), 1992, pp. 390-392 entitled "Electrodeposited composites - a review on new technologies for aerospace and other fields" gives an overview of methods for the electrochemical deposition of layers.

DE 101 13 767 A1 discloses an electroplating method.

DE 39 43 669 C2 discloses a method and an apparatus for electrolytic surface treatment, in which the parts of the compound used for coating are intimately mixed by vibratory movement and/or rotary movement, so that a uniform electrolytic layer is deposited.

Other electrolytic coating methods are known from GB 2 167 446 A, EP 443 877 A1 and from the article by J. Zahavi et al. in Plating and Surface Finishing, Jan. 1982, pp. 76 ff "Properties of electrodeposited composite coatings", in which undissolved particles are used in the electrolyte in order for these particles also to be deposited in the layer.

Electrochemical Society Proceedings Vol. 95-18, pp. 543 ff von Sarhadi et al. entitled "Development of a low

current density electroplating bath ..." describes the use of baths which contain cobalt, nickel or iron compounds.

US-A 6,375,823 B1 describes an electrolytic coating method in which an ultrasound probe is used.

DE 195 45 231 A1 describes a method for the electrolytic deposition of metal layers which uses a pulsed current or pulsed voltage method. However, this is only employed to reduce ageing phenomena in deposition baths.

US 2001/00 54 559 A1 discloses an electrolytic coating method which uses pulsed currents to prevent the undesired evolution of hydrogen during electrolytic coating of metals.

DE 196 53 681 C2 discloses a method for the electrolytic deposition of a pure copper layer which uses a pulsed current or pulsed voltage method.

DE 100 61 186 C1 describes a method for electrolytic deposition which uses periodic current pulses.

In the article entitled "Electrodeposited composite coatings for protection from high temperature corrosion" in Trans IMF 1987, 65, 21ff, V. Sova describes an electrolytic deposition method, in which particles which are not dissolved in the electrolyte are used for the layer which is to be applied. The article also describes the use of pulsed currents.

Layers applied using the known methods have poor adhesion to the substrate under the conditions of some intended uses. Moreover, it is only possible to deposit materials with a constant composition.

Therefore, it is an object of the invention to overcome the above problems.

The object is achieved by a method for the deposition of an alloy on a substrate in accordance with claim 1.

The use of pulsed currents or the generation of graduated layers improves the bonding of layers to the substrate and/or the deposition rate.

Further advantageous configurations of the method are listed in the claims.

An exemplary embodiment of the invention is explained in more detail in the figures, in which:

Figure 1 shows an apparatus for carrying out the method according to the invention, and
Figure 2 shows a sequence of a current/voltage pulse which is used for a method according to the invention.

Figure 1 shows an apparatus 1 for carrying out the method according to the invention.
An electrolyte 7, an electrode 10 and a substrate 13 that is to be coated are arranged in a vessel 4. The substrate 13 which is to be coated is, for example, a combustion chamber lining, a housing part or a turbine blade or vane, made from a nickel-, cobalt- or iron-base superalloy, of a gas or steam turbine, which,

however, may also already have a layer on the substrate (MCrAlY).

The substrate 13 and the electrode 10 are electrically conductively connected to a current/voltage source 16 via electrical supply conductors 19. The current/voltage source 16 generates pulsed electric currents/voltages (Fig. 2).

The electrolyte 7 contains the individual constituents of an alloy which are to be deposited on the substrate 13. For example, the electrolyte 7 contains a first constituent 28 and a second constituent 31 of an alloy.
The constituents 28, 31 are deposited on the substrate 13 by suitable selection of the process parameters (Fig. 2). Gradients can also be produced in the chemical composition of the layer to be produced by suitable selection of the process parameters.
By way of example, an alloy MCrAlY, in which M stands for at least one element selected from the group consisting of iron, cobalt or nickel, is deposited on the substrate 13. The alloying elements Cr, Al, Y and any further elements are introduced either by the addition of suitable soluble salts to the electrolyte or by suspending fine-grain, insoluble powders in the electroplating bath, with these powders being deposited as solid particles. By way of example, at least two constituents are dissolved, for example in the form of salts, in the electrolyte 7.
The layer can be homogenized or densified by a subsequent thermal process, or defined phases can be established in the layer.

An ultrasound probe 22, which may be arranged in the electrolyte 7 and is controlled by an ultrasound transmitter 25, improves the hydrodynamics and the mixing of the constituents 28, 31 in the region of the substrate 13, so as to accelerate the deposition process.

The oscillation frequency is, for example, above 1 kHz.

The current/voltage level, the pulse duration and the interpulse period are defined for at least one and in particular for every constituent 28, 31 of the alloy.

Figure 2 shows an example of a series of repeating current pulses (40).
A sequence 34 comprises at least two blocks 37. In Figure 2, there are four blocks 37. However, there may also be three, five or more blocks 37.
Each block 37 comprises at least one current pulse 40. In Figure 2, each block comprises three, four or six current pulses 40. However, it is also possible to use two, five or more than six current pulses 40 per block 37. A current pulse 40 is characterized by its duration t_{on}, the intensity I_{max} and its shape (square-wave, delta-wave, etc.). The pauses between the individual current pulses 40 (t_{off}) and the pauses between the blocks 37 are also important process parameters.
The sequences may likewise change over the course of time.

The sequence 34 consists, for example, of a first block 37 with three current pulses 40, between each of which there is a pause. This is followed by a second block 37, which has a higher or lower current intensity, since it is adapted to a different constituent 28, 31, and comprises six current pulses 40. After a further pause, there then follow four current pulses 40 in the opposite direction, i.e. with an altered polarity, in order to correct the alloy composition, the hydrogen desorption or to effect activation.
Each block 37 may therefore include a different number of current pulses 40, pulse durations t_{on} or interpulse periods t_{off}.

The sequence 34 is concluded by a further block 37 of four current pulses.
The sequence can be repeated a number of times.

The individual pulse times t_{on} are preferably of the order of magnitude of approximately 1 to 100 milliseconds. The duration of the block 37 is of the order of magnitude of up to 10 seconds, which means that up to 5000 pulses are emitted in a block 37.

It is optionally possible for a low potential (base current) to be applied both during the pulse sequences and during the interpulse period. This avoids interruption to the electro-deposition, which can cause inhomogeneities.

The parameters of a block 37 are adapted to a constituent 28, 31 of the alloy, in order to achieve the optimum deposition of this constituent 28, 31. These parameters can be determined in individual tests. An optimized block 37 leads to an optimized deposition of the constituent optimized for this block 37, i.e. the duration and nature of the deposition are improved. The other constituents are likewise also deposited.
This optimization can be carried out for at least one further constituent, for example all the constituents 31 of the alloy. The result is that the composition of the constituents 28, 31 is optimized.

The level of the constituents 28, 31 in the layer to be applied can be defined, for example, by the duration of the individual blocks 37.

Gradients can likewise be produced in the layer. This is done by correspondingly lengthening or shortening the duration of the block 37, the current/voltage intensity or the number of pulses 40 per block which is optimally adapted to a constituent 28, 31

(i.e. the sequence 34 is altered).
A sequence 34 can also be altered if, for example, the deposition rate of a constituent 28, 31 alters over the course of time on account of the layer which has already been deposited.

It is also possible for further non-alloying constituents, such as for example secondary phases, to be contained in the electrolyte 7 and deposited.